

## PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P 63404	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/06534	International filing date (day/month/year) 20.06.2003	Priority date (day/month/year) 21.06.2002
International Patent Classification (IPC) or both national classification and IPC C07F7/18		
Applicant HONEYWELL SPECIALTY CHEMICALS SEELZE GMBH et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 12 sheets.

## 3. This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  21.01.2004	Date of completion of this report  27.09.2004
Name and mailing address of the International preliminary examining authority:   European Patent Office D-80293 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Zellner, A  Telephone No. +49 89 2399-8078  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/06534**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-26 as originally filed

**Claims, Numbers**

1-50 received on 20.07.2004 with letter of 16.07.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/06534**

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	1-50
	No: Claims	
Inventive step (IS)	Yes: Claims	1-50
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-50
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/06534

1. The following documents (D) are referred to in this communication; the numbering will be adhered to in the rest of the procedure:

D1: WO 2003 044600 A (USA)  
D2: WO 2003 044077 A (HONEYWELL INTERNATIONAL INC., USA)  
D3: WO 2000 077575 A (HONEYWELL INTERNATIONAL INC., USA)  
D4: US-B1-6 365 765 (BALDWIN, TERESA ET AL)  
D5: DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; UNO, SEIJI ET AL: 'Positive-working photoresist composition for upper resist layer of composite two-layer resist' retrieved from STN Database accession no. 134:318673 XP002255969 & JP 2001 109150 A (FUJI PHOTO FILM CO., LTD., JAPAN) 20 April 2001 (2001-04-20)

2. The present application relates to silyl alkyl esters of general formula (I).
3. The amendments filed with letter dated 16.07.2004 were found to be in accordance with the requirements of Art. 34(2)(b) PCT.

**item V**

4. Novelty (Art. 33(2) PCT)

None of the documents D3-D5 discloses compounds of general formula (I) according to present claims 10 or 18 nor the method according to amended claim 1. Novelty for the claimed subject-matter can thus be acknowledged. The requirements of Art. 33(2) PCT are thus met.

5. Inventive step (Art. 33(3) PCT)

- 5.1. The method according to present claim 1 leads to known compounds (10 in D3 and D4). According to D3/D4 (same priority) the carboxylic acid is used as a starting material whereas the metal salt is required according to amended claim 1. When compared to D3, yield and purity are considerably higher (see examples 1a and 1b). Since the cited prior art does not appear to suggest the use of the carboxylic acid salt, presence of an inventive step for claim 1 can be acknowledged.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/06534

5.2. Claims 10 and 18 relate to compounds of formula I. Due to the limitation of  $R_4$  and  $R_5$  to hydrogen and  $n = 3-5$  (claim 10) and to phenanthrene (claim 18), novelty can be acknowledged. Applicant has shown by way of comparable examples that compounds having  $n=3$  have a higher thermal stability than compound 10 of D3, for which  $n=1$  (see test report filed with letter dated 16.07.2004). Further comparative data indicate that compounds having a phenanthrene structure absorb at a lower wavelength than a comparable anthracene compound (10 of D3). This leads to an advantage in the production of semiconductors, i.e. the possibility of using shorter wavelengths for more narrow linewidths. Since none of the cited documents appears to lead the skilled person to the structural changes in order to obtain the said advantageous effects, the presence of an inventive step can be acknowledged for claims 10 and 18.

5.2. Independent claims 25, 34, 40, 41, 44 and 48 relate to compounds of claims 10 or 18 and thus fulfil the requirements of Art. 33(3) PCT as well.

6. Industrial applicability (Art. 33(4) PCT)

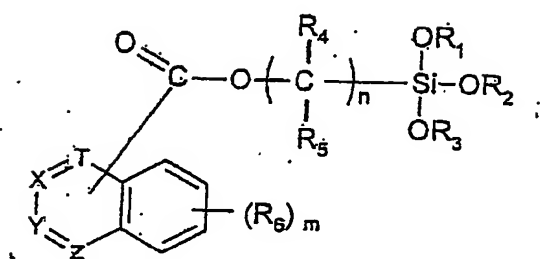
Can be acknowledged for claims 1 to 45.

7. Documents D1 and D2 were published after the priority date of the present application but before its international filing date. Their content would be considered as forming part of the state of the art if the priority of the present application was found to be invalid.

8. The description is not yet in accordance with the amended set of claims (Art. 6 PCT).

Claims

1. Method for the preparation of a silyl alkyl ester having the Formula (I)



(I)

in which.

$R_1$ ,  $R_2$ , and  $R_3$  are equal or different and represent alkyl, aryl and heteroaryl,

$R_4$  and  $R_5$  are equal or different and represent hydrogen, halogen, alkyl, aryl and heteroaryl,

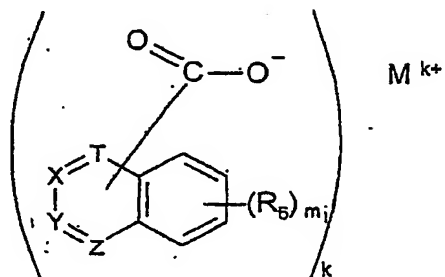
$n$  is an integer from 1 to 10,

$R_6$  is a substituent selected from halogen, alkyl, aryl, heteroaryl, hydroxy, alkoxy, aryloxy, substituted and unsubstituted amino group, carboxy group, carboxylic acid ester group, carboxylic acid amide group, sulfonic acid group, sulfonic acid ester group, sulfonyl, thio, thioether and nitro,

$m$  is an integer from 0 to 4,

T, X, Y and Z each represent carbon,  
 a benzo group, which is m-fold substituted with  $R_6$  or  
 which is unsubstituted, is condensed on one of the bonds  
 T-X, X-Y or Y-Z to form a trinuclear aromatic ring system,  
 wherein the silyl alkyl ester group is substituted at the  
 middle ring of said trinuclear aromatic ring system,

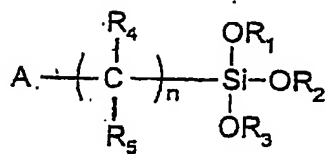
wherein a carboxylic acid salt of Formula (II)



.(II)

in which k is an integer from 1 to 4 and M is a metal,

is reacted with an organosilicon compound of Formula (III)



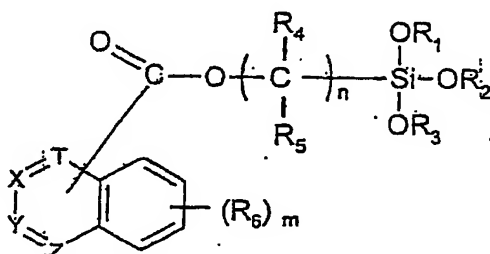
(III)

in which A represents a nucleofugal leaving group.

2. Method according to Claim 1, wherein the metal M is selected from the groups Ia, IIa, IIIa, IVa, Ib, IIb, IVb and VIIb of the periodic table.
3. Method according to Claim 1 or 2, wherein  $k = 1$ .
4. Method according to any one of Claims 1 to 3, wherein M is selected from metals of Group Ia.
5. Method according to any one of Claims 1 to 4 wherein the metal M is selected from lithium, sodium and potassium.
6. Method according to any one of Claims 1 to 5 wherein the metal M is sodium and/or potassium and particularly potassium.
7. Method according to any one of Claims 1 to 6 wherein the nucleofugal leaving group A represents halogen, preferably chlorine and/or bromine and yet more preferably chlorine.



8. Method according to any one of Claims 1 to 7 wherein the carboxylic acid salt of Formula (II) is reacted with the organosilicon compound of Formula (III) in a solvent or solvent mixture, from which the metal salt of the formula  $MA_x$  formed is precipitated.
9. Method according to Claim 8, wherein as solvent or solvent mixture, N,N-dimethylformamide and/or N,N-dimethylacetamide is used.
10. Silyl alkyl ester having the formula (I)



(I)

wherein

$\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are equal or different and represent alkyl, aryl and heteroaryl,

$\text{R}_4$  and  $\text{R}_5$  each represent hydrogen,

$n$  is an integer from 3 to 5,

$\text{R}_6$  is a substituent selected from halogen, alkyl, aryl, heteroaryl, hydroxy, alkoxy, aryloxy, substituted and unsubstituted amino group, carboxy group, carboxylic acid ester group, carboxylic acid amide group, sulfonic acid

group, sulfonic acid ester group, sulfonyl, thio, thioether and nitro,

m is an integer from 0 to 4,

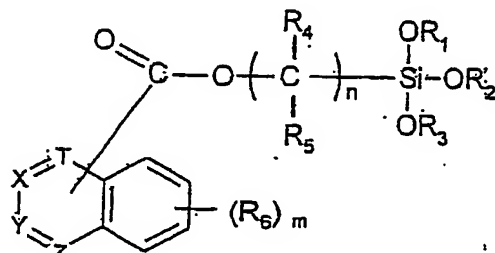
T, X, Y and Z each represent carbon,

a benzo group, which is substituted m-fold with  $R_6$  or which is unsubstituted, is condensed on one of the bonds T-X, X-Y or Y-Z to form a trinuclear aromatic ring system, wherein the silyl alkyl ester group is substituted at the middle ring of said trinuclear aromatic ring system.

11. Silyl alkyl ester according to Claim 10, wherein  $R_1$ ,  $R_2$ , and  $R_3$  each represent alkyl.
12. Silyl alkyl ester according to Claim 10 or 11, wherein  $R_1$ ,  $R_2$ , and  $R_3$  are selected, independently of one another, from methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-methylpropyl, 1-methylpropyl and 1,1-dimethylethyl.
13. Silyl alkyl ester according to any one of Claims 10 to 12, wherein  $R_1$ ,  $R_2$ , and  $R_3$  each represent methyl or ethyl.
14. Silyl alkyl ester according to any one of Claims 10 to 13, wherein a benzo group, which is m-fold substituted with  $R_6$  or which is unsubstituted, is condensed on the X-Y bond.
15. Silyl alkyl ester according to Claim 14, wherein an unsubstituted benzo group is condensed on the X-Y bond and  $m=0$ .
16. Silyl alkyl ester according to any one of Claims 10 to 13, wherein a benzo group, which is m-fold substituted with  $R_6$  or which is unsubstituted, is condensed on either the T-X or Y-Z bond.

17. Silyl alkyl ester according to Claim 16, wherein an unsubstituted benzo group is condensed on either the T-X or Y-Z bond and  $m=0$ .

18. Silyl alkyl ester having the formula (I)



(I)

wherein

$R_1$ ,  $R_2$ , and  $R_3$  are equal or different and represent alkyl, aryl and heteroaryl,

$R_4$  and  $R_5$  are equal or different and represent hydrogen, halogen, alkyl, aryl and heteroaryl,

$n$  is an integer from 1 to 10,

$R_6$  is a substituent selected from halogen, alkyl, aryl, heteroaryl, hydroxy, alkoxy, aryloether, substituted and unsubstituted amino group, carboxy group, carboxylic acid ester group, carboxylic acid amide group, sulfonic acid group, sulfonic acid ester group, sulfonyl, thio, thioether and nitro,

$m$  is an integer from 0 to 4,

T, X, Y and Z each represent carbon,

a benzo group, which is substituted m-fold with  $R_6$  or which is unsubstituted, is condensed on either the T-X or Y-Z bond to form a trinuclear aromatic ring system, wherein the silyl alkyl ester group is substituted at the middle ring of said trinuclear aromatic ring system.

19. Silyl alkyl ester according to Claim 18, wherein  $R_1$ ,  $R_2$ , and  $R_3$  each represent alkyl.
20. Silyl alkyl ester according to Claim 18 or 19, wherein  $R_1$ ,  $R_2$ , and  $R_3$  are selected, independently of one another, from methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-methylpropyl, 1-methylpropyl and 1,1-dimethylethyl.
21. Silyl alkyl ester according to any one of Claims 18 to 20, wherein  $R_1$ ,  $R_2$ , and  $R_3$  each represent methyl or ethyl.
22. Silyl alkyl ester according to any one of Claims 18 to 21, wherein  $R_4$  and  $R_5$  each represent hydrogen.
23. Silyl alkyl ester according to any one of Claims 18 to 22, wherein n is an integer from 1 to 5, particularly from 1 to 3, yet more preferably 1 or 3 and most preferably 3.
24. Silyl alkyl ester according to any one of Claims 18 to 23, wherein an unsubstituted benzo group is condensed on either the T-X or Y-Z bond and  $m=0$ .
25. Composition which comprises at least one silyl alkyl ester according to any one of Claims 10 to 24 and at least one further reactive silane.
26. Composition according to Claim 25, wherein the reactive silane is selected from alkoxy silanes and halogen silanes, particularly chlorosilanes.

27. Composition according to Claim 25 or 26, **wherein** the reactive silane is selected from triethoxysilane (HTEOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), dimethyldiethoxysilane, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS), trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane (PTEOS), phenyltrimethoxysilane (PTMOS), diphenyldiethoxysilane, diphenyldimethoxysilane, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methyldichlorosilane, dimethyldichlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane and chlorophenyltrimethoxysilane.
28. Composition according to any one of Claims 25 to 27, **wherein** the reactive silane is selected from triethoxysilane (HTEOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS), phenyltriethoxysilane (PEOS) and phenyltrimethoxysilane (PTMOS).
29. Composition according to any one of Claims 25 to 28, **which** comprises a solvent or solvent mixture.
30. Composition according to Claim 29, **wherein** the solvent or solvent mixture comprises at least one component selected from water, linear or branched alkyl alcohol having 1 to 6 carbon atoms, linear or branched ketone having 1 to 6 carbon atoms, linear or branched carboxylic acid ester having 1 to 6 carbon atoms and linear or branched carboxylic acid amide having 1 to 6 carbon atoms.

31. Composition according to Claim 29 or 30, **wherein** the solvent or solvent mixture comprises at least one component selected from water, acetone, 1-propanol, 2-propanol, butanol, methylisobutylketone, methoxypropanol, propoxypropanol, ethyl acetate and propyl acetate.
32. Composition according to any one of Claims 25 to 31, **which** comprises an aqueous solution of at least one protonic acid and/or an aqueous solution of at least one acid anhydride.
33. Composition according to Claim 32, **wherein** the protonic acid is nitric acid.
34. Method for the preparation of a polysiloxane composition, **wherein** a composition according to any one of Claims 25 to 33 is provided and the silyl alkyl ester is condensed with the reactive silane.
35. Method according to Claim 34, **wherein** the condensation of the silyl alkyl ester with the reactive silane is carried out by heating.
36. Method according to Claim 35, **wherein** the composition is heated for 1 to 24 hours, more preferably for 1 to 10 hours and yet more preferably for 2 to 6 hours at a temperature of 20 to 100°C, more preferably from 40 to 80°C and yet more preferably from 60 to 80°C.
37. Method according to any one of Claims 34 to 36, **wherein** during the condensation, polysiloxane having a low molecular weight and degree of cross-linking is formed, which is dissolved or suspended in the solvent or solvent mixture.

38. Method according to any one of Claims 34 to 37, wherein during or after the condensation, a diluting solvent is added.
39. Method according to Claim 38, wherein the diluting solvent comprises at least one component selected from methanol, ethanol, 2-propanol, butanol, acetone, propyl acetate, ethyl lactate, propylene glycol propyl ether, diacetone alcohol and methoxypropanol.
40. Polysiloxane composition, which is obtainable by a method as defined in any one of Claims 34 to 39.
41. Coated substrate, which is obtainable by a method comprising applying the composition as defined in any one of claims 25 to 33 or the polysiloxane composition as defined in claim 40 to the substrate and heating the substrate with the composition or polysiloxane composition applied thereon.
42. Coated substrate according to claim 41, wherein applying of said composition or said polysiloxane composition is performed by means of spin techniques.
43. Coated substrate according to claim 41 or 42, wherein the substrate is selected from a semiconductor device, a silicon-wafer, a glass plate and a metal plate.
44. Use of a composition as defined in any one of Claims 25 to 33 or of a polysiloxane composition as defined in Claim 40 for the preparation of a coating on a substrate.
45. Use according to Claim 44, wherein the composition or the polysiloxane composition is applied to the substrate and

the substrate with said composition or polysiloxane composition applied thereon is heated.

46. Use according to Claim 44 or 45, wherein the composition or the polysiloxane composition is applied to the substrate by means of spin techniques.
47. Use according to any one of Claims 44 to 46, wherein the substrate is a semiconductor device or a silicon wafer.
48. Method for the photolithographic production of an integrated circuit pattern comprising the steps of:
  - (a) radiating a stack through a mask, said stack comprising the lower substrate, an upper photoresist layer, at least one anti-reflective layer formed from the composition as defined in any one of claims 25 to 33 or from the polysiloxane composition as defined in claim 40, and optionally at least one further layer to be structured, each being located between said substrate and said photoresist layer,
  - (b) developing the exposed stack to produce openings in said photoresist layer,
  - (c) etching a first pattern through said openings in said at least one anti-reflective layer and optionally at least one further layer to be structured, and



(d) stripping off said photoresist layer, at least one anti-reflective layer and optionally at least one further layer to be structured to produce the integrated circuit pattern.

49. Method according to claim 48, wherein the substrate is a semi-conductor device or a silicon wafer.

50. Method according to claim 48 or 49, wherein in step (a) the stack is radiated with ultraviolet light having a wavelength of less than 260 nm, particularly 193 nm or 248 nm.